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DEPARTMENT OF MICROELECTRONICS

TESTING OF HYDROGEN SENSORS BASED ON ORGANIC MATERIALS

TESTOVÁNÍ ORGANICKÝCH VODÍKOVÝCH SENZORŮ

MASTER´S THESIS
DIPLOMOVÁ PRÁCE

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Abstract

This thesis is focused on topic of safety hydrogen sensors. Theory of hydrogen sensors and main sensor principles are discussed. Methodology for testing of organic hydrogen sensors developed and fabricated at the Faculty of Chemistry of Brno University of Technology is outlined. A set of tests is done for the most promising organic material. Also, temperature regulator for ceramic sensor platform is designed.

Abstrakt

Práce je zaměřena na problematiku bezpečnostních vodíkových senzorů. Základní principy a teorie vodíkových senzorů je rozebrána v první části práce. Je navržena metodologie testování organických vodíkových senzorů vyvinutých a vyrobených na Fakultě Chemické Vysokého Učení Technického v Brně. Nejslibnější organický material byl testován. V závěrečné části byl navržen teplotní regulátor pro použití s keramickou senzorovou platformou.

Key words: hydrogen, sensor, testing, organic, diketopyrrolopyrrole, temperature regulator

Klíčová slova: vodík, sensor, testování, organický, diketopyrrolopyrrol, teplotní regulátor

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Supervisor prof. Ing. Jaroslav Boušek, CSc.

DECLARATION

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Student's signature

ACKNOWLEDGEMENT

I would like to express gratitude to my supervisor, prof. Ing. Jaroslav Boušek, CSc. for guidance and help with this thesis. Also, I would like to thank doc. Ing. Ota Salyk, CSc. for letting me take part in the sensor testing at the Faculty of Chemistry.

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1. Introduction

Current need for clean, renewable energy puts emphasis on development of hybrid general purpose engines. Hydrogen is fuel not only for aerospace, but also possibly for common use in transportation, where only emissions are water. The public is, however, concerned about the safety of hydrogen, which is essential due to the nature of hydrogen.

Reliable hydrogen sensors are essential for safety in hydrogen applications such as semiconductor manufacturing (process control and leak testing) and hybrid engines.

The need for robust, affordable, and compact hydrogen safety sensors is driving the development of new sensor technology. Current production sensors can provide repeatable and accurate hydrogen sensing; however these sensors are costly and often not ideally selective to hydrogen[1]. Transportation applications will further increase the demand for cheap, simple, reliable, and low-cost hydrogen gas sensors to guard against possible accidents.

Main goal of this project is to design a simple facility for testing of commercially available hydrogen sensors mainly for application in the automotive industry.

Currently, energy production is dependent mostly on fossil fuels. This brings up the problem with pollution. Also, access to these is limited. This leads to usage of alternative sources of energy. The power potential of photovoltaic technologies, for example, grows rapidly and has more than 20% increase each year. The efficiency of the most used technology, based on single junction silicon solar cell, is to time about 20% and new system based on multi-junction cells are emerging promising to break 30% efficiency limit of single junction PV cell. Use of concentrator systems ensure the lowering of capital costs. Unfortunately, like other renewable energy sources, PV cells have variable output. The peak power can be quite high, but there are also large periods without any power supply. The storage of the energy is possible using rechargeable batteries but in fact this can be effectively ensured only for limited capacity. Moreover the storage time is relatively short and batteries are expensive. [2]

Such energy can be used to produce hydrogen, in which it can be stored for unlimited time, easily transported and used in fuel cells, or directly used in engines as fuel. The only emission in hydrogen powered engines or fuel cells is water. From this point of view is hydrogen the ideal storage medium for energy solving both problems with access to energy and pollution. Currently, major car manufacturers put emphasis on research and development of hydrogen car prototypes.

To use hydrogen in large scale and mainly in hydrogen-powered cars new facilities must be implemented to replace today's gasoline-based infrastructure with that of hydrogen. This will bring serious safety problems because hydrogen gas is not only highly explosive with flammability limit in air about 4% but also invisible and non-odorant. In comparison in other fuels, methane gasoline for example, hydrogen has also much lower ignition energy. Odorants that might be added to hydrogen can diminish the danger only partially. Moreover such substances may possibly interact with catalysts used in fuel cells. For safety of hydrogen-power facilities a sensitive leak detection system is therefore crucial. The preferred method to detection hydrogen leaks in storage tanks is to integrate sensors on the external surface of the tanks. [3]

1.1. Hydrogen

Hydrogen is a colorless, odorless and tasteless gas, therefore undetectable by human senses. It is lighter than air and mixes with air to create a flammable and explosive mixture. Lower flammable limit (LFL, also lower explosion limit - LEL) of hydrogen is 4% of volume, while Upper flammable limit (UFL) is 75% of volume.

Furthermore, small size of the molecule causes the gas to diffuse rapidly and permeate easily through various materials. This makes hydrogen a substance very difficult to store and use safely.

1.2. Hydrogen sensors

Sensitivity, accuracy, selectivity and fast response are main characteristics of a hydrogen sensor. On the other hand the size and price of the sensor has to be respected. The selection of sensor type depends on its application.

Main causes of faulty signals in hydrogen sensors include environmental causes such as dust, dirt, humidity, fluctuating temperature and contamination. Hydrogen sensors are mostly baffled by presence of hydrocarbon. All these can be simulated during testing to determine the suitability of a certain sensor for the given application.

1.2.1. Requirements

Standard requirements:

- Reliability: Functionality should be easily verifiable.
- Performance: Detection 0.5% hydrogen in air or better
- Response time < 1 second
- Lifetime: At least the time between scheduled maintenance
- Cost: Goal is $5 per sensor and $30 per controller

Additional requirements:

- Measurement range coverage of 0.1%–10.0% concentration
- Operation in temperatures of -30°C to 80°C
- Accuracy within 5% of full scale
- Function in an ambient air gas environment within a 10%–98% relative humidity range
- Resistance to hydrocarbon, carbon monoxide and other interference
- Lifetime greater than 10 years[4]

1.3. Types of hydrogen sensors

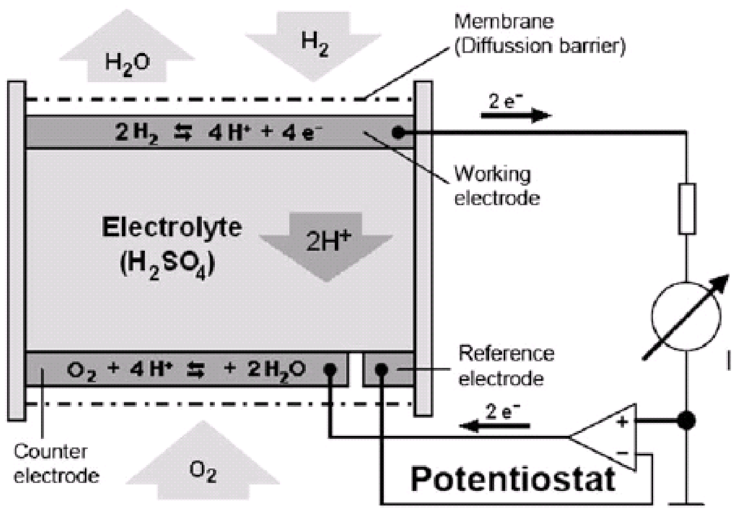
Sensors can be categorized into six main types: electrochemical, metal oxide, pellistor, thermal conductivity, palladium and palladium alloy film, and optical devices.

1.3.1. Electrochemical sensors

These sensors usually consist of three electrodes, an electrolyte and a selective, semi-permeable membrane.

Reactions on the sensor surface cause a potential difference between the electrodes and H_2 concentration is represented by this potential difference.

A third, reference electrode is added to the cell to improve stability of measurements.



Picture 1: Electrochemical sensor {9}

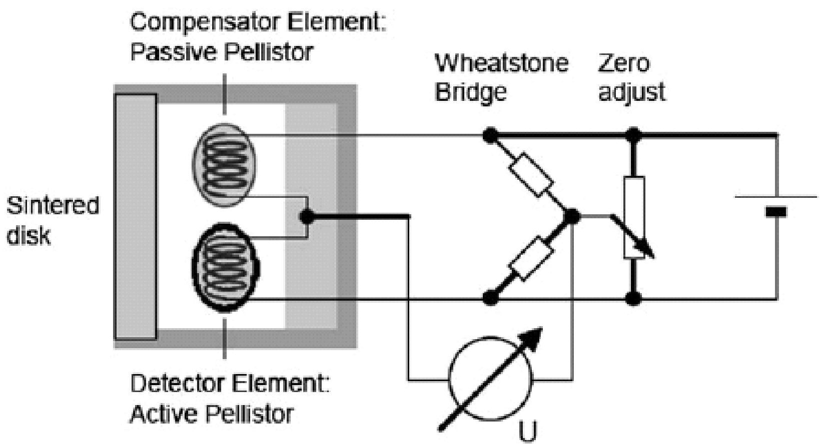
These hydrogen sensors are widely commercially available. Electrolyte development, improved sensitivity and faster response times are currently the main concern in the electrochemical sensors.

Low power consumption is a big advantage in the automotive industry. However, sensors employing a liquid electrolyte cannot be operated or stored at low pressures or at sub-zero temperatures.

1.3.2. Catalytic hydrogen sensors

A catalytic sensor detects hydrogen based on the temperature change. This temperature change occurs due to exothermic oxidation on heated surface.

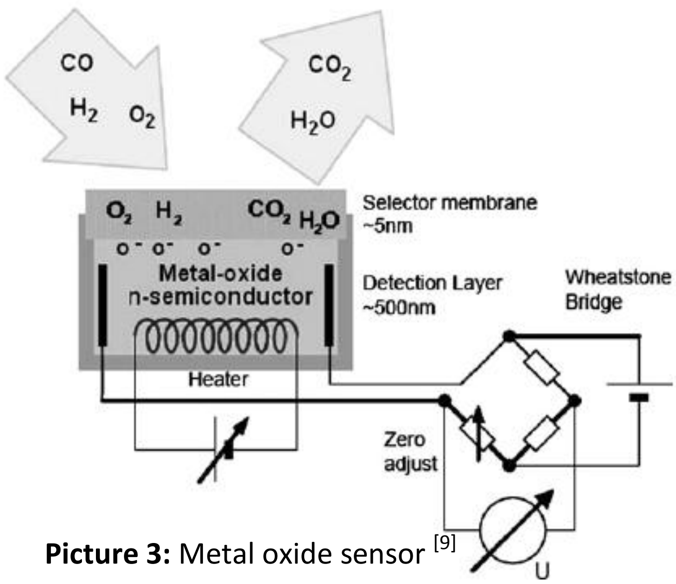
The surface consists of two pellistors, platinum wires embedded in ceramic beads, interconnected via a Wheatstone bridge. One pellistor is coated in a catalyst material which only catalyzes the oxidation reaction of hydrogen, the surface of the other pellistor is inertised. The pellistors are heated by the current to 500–550°C.



Picture 2: Catalytic hydrogen sensor

1.3.3. Metal oxide sensors

Two different types of sensors are commonly referred to as MOS. The first type has a structure consisting of a metal, insulator and semiconductor layer (MIS), in most cases, the insulator layer is formed by oxide, therefore MOS sensor. The function is based on charge building up and changing the



Picture 3: Metal oxide sensor [9]

function of the sensing layer. The sensing layer is usually formed by some noble metal or alloy (palladium based alloys). This structure can work as a capacitive sensor, FET transistor or Shottky diode.

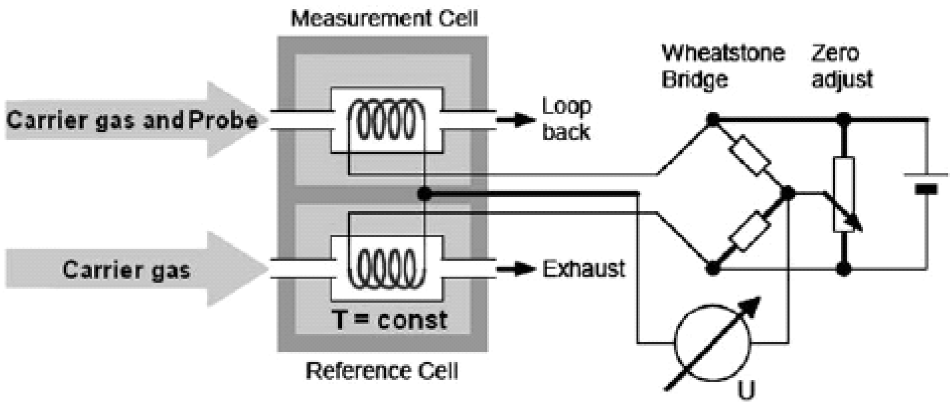
Second type (shown in picture) uses oxide layer as the sensing layer. Function is based on the idea, that presence of reducing gases like hydrogen and carbon dioxide leads to diffusion through the pores into the sensing layer and reaction with adsorbed oxygen.

These sensors have a heated metal-oxide layer with semiconductive properties, where hydrogen is adsorbed.

These sensors are small, easily mass-produced and low cost, but also have many disadvantages (selectivity and response time problem).

1.3.4. Thermal conductivity sensors

Gaseous hydrogen has the highest thermal conductivity of all known gases. This feature is often used for detection and monitoring of hydrogen.



Picture 4: Thermal conductivity sensor[9]

Two identical cells are placed into environment with constant temperature, one is put into flow of pure carrier gas, the other one is in flow of carrier gas and hydrogen. Hydrogen and carrier gas will extract more heat from the cell than only carrier gas. The temperature difference causes resistance difference between the cells, which are connected to a Wheatstone bridge, causing measurable imbalance.

This type is unable to measure low concentrations, but due to measurement measure to up to 100% H_2.

1.3.5. Palladium sensors

The hydrogen response of Pd is thought to be based on three factors: hydrogen adsorption on the palladium surface, hydrogen diffusion into the palladium, and formation of dissociated hydrogen dipoles at the palladium–insulator interface. Among candidate metals, platinum has a higher catalytic activity than Pd. Platinum is thought to be stable because of its low hydrogen diffusion as compared to palladium.[5]

Hydrogen sensors and hydrogen-activated switches are fabricated from arrays of mesoscopic palladium wires. Exposure to hydrogen gas caused a rapid (less than 75 milliseconds) reversible decrease in the resistance of the array that correlated with the hydrogen concentration over a range from 2 to 10%. The sensor response appears to involve the closing of nanoscopic gaps or "break junctions" in wires caused by the dilation of palladium grains undergoing hydrogen absorption. Wire arrays in which all wires possessed nanoscopic gaps reverted to open circuits in the absence of hydrogen gas. Submicrometer wires of palladium embedded in a polymer matrix are shown to decrease their resistance at room temperature in the presence of hydrogen, unlike bulk palladium, which becomes more resistive as the hydride forms. Hydrogen adsorption lowers the resistance by expanding microcrystallites in the wires, which then heals tiny "break junctions" in the wire. These effects are seen even when gases that normally poison hydrogen sensing were present, including O_2, CO, and CH_4. The rapid response and low power requirements suggest their use as sensors and switches. [6]

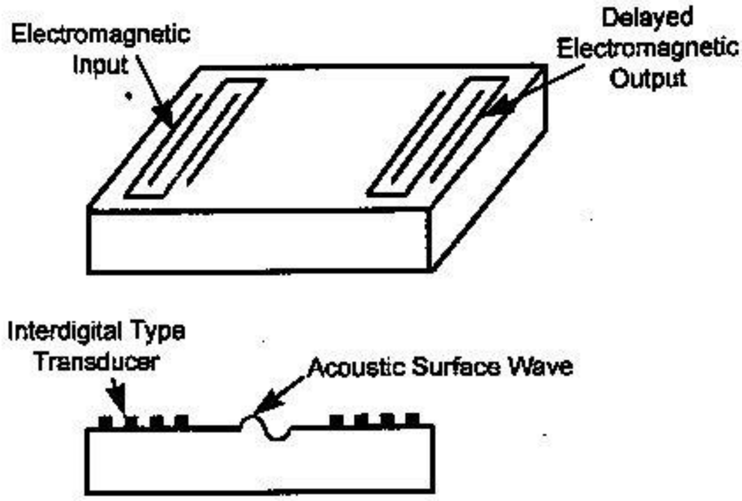
Optical fibre surface plasmon resonance (SPR) sensor has been developed for the detection of hydrogen leakages. A thin palladium layer deposited on the bare core of a multimode fibre was used as the transducer. In this device, modification of the SPR is due to variation in the complex permittivity of palladium in contact with gaseous hydrogen. This effect is enhanced by using selective injection of high-order modes in the fibre via a collimated beam with non-normal incidence on the input end of the fibre. Measurements of concentrations as low as 0.8% of hydrogen in pure nitrogen have been found to be possible. The response time varies between 3 s for pure hydrogen and 300 s for the lowest concentrations. Such a large range can be explained by the two different crystallographic phases of the palladium-hydrogen system. Moreover, the response of the sensor is dependent on the length of the sensing area. In preliminary experiments, it has been possible to split the sensing area in order to achieve a two-point detection device. [7]

1.3.6. Surface Acoustic Wave

SAW gas sensors are especially attractive because of their remarkable sensitivity due to changes of the boundary conditions of the propagating wave, introduced by the interaction of an active thin film with specific gas molecules.

This unusual sensitivity results from the simple fact that most of the wave energy is concentrated near the crystal surface within one or two wavelengths.

Consequently, the surface wave is in its first approximation highly sensitive to any changes of the physical or chemical properties.



Picture 5: SAW sensor [10]

2. Testing facility

2.1. Expectations

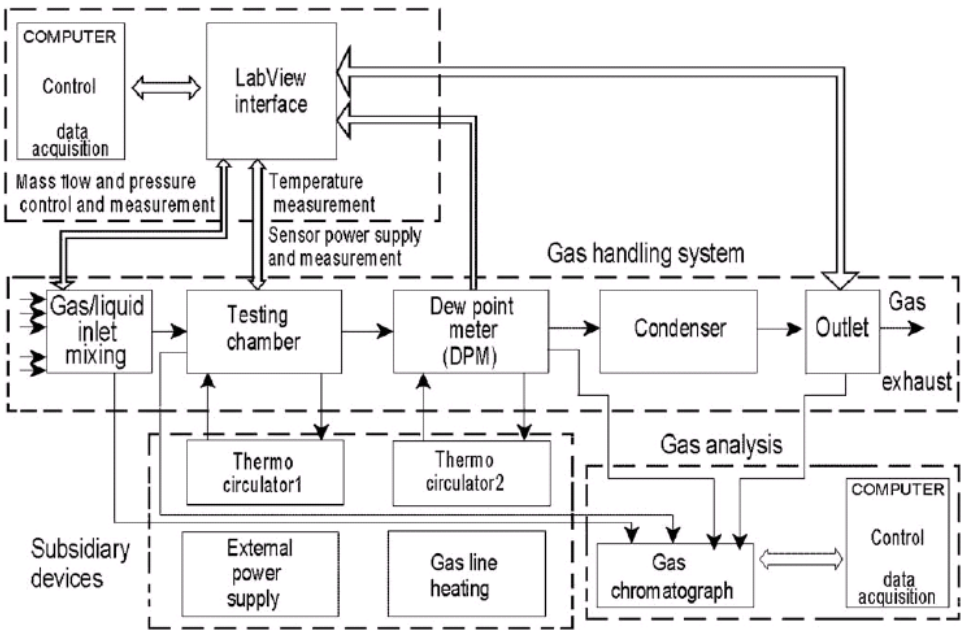
The basic function of testing facility for hydrogen sensors is providing conditions for testing. This means defined hydrogen concentration, pressure, temperature and humidity, eventually concentration of other gases for cross-sensitivity and contamination testing.

Among other functions is the possibility to measure response of sensor output to change of temperature, hydrogen concentration, humidity or contamination.

On the other hand, the goal of this project is to design a simple, low cost and easy to use facility. This is the limit of possibilities.

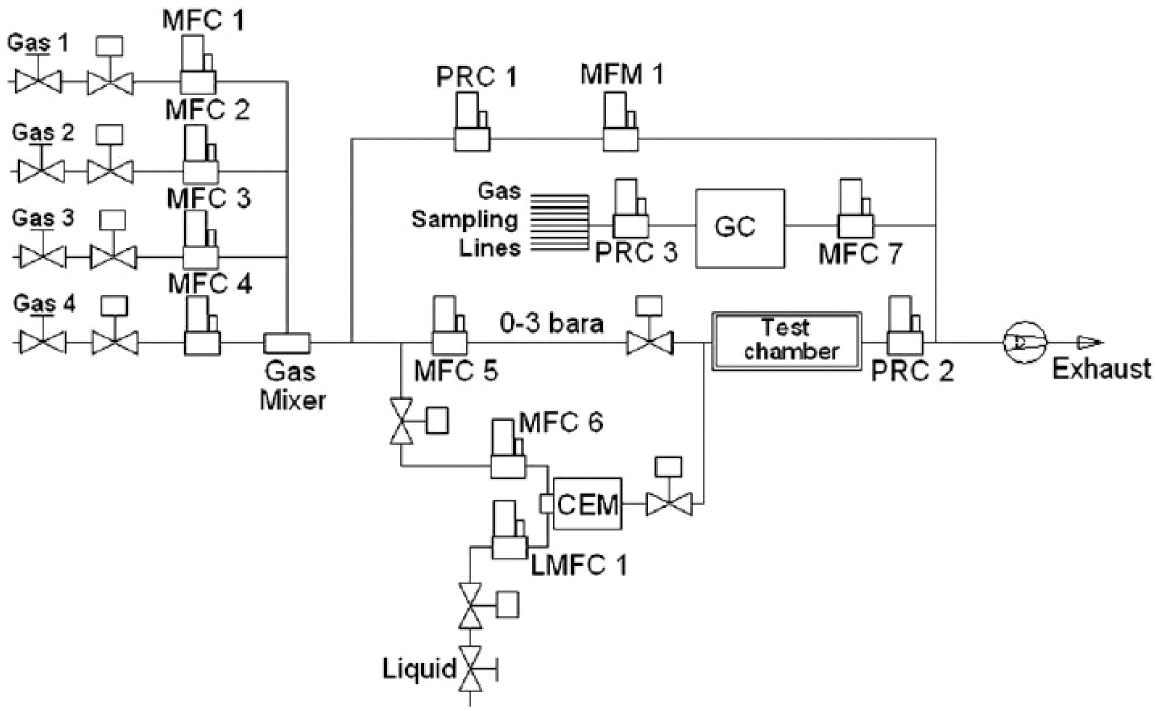
2.1.1. Dynamic system

Dynamic system is the ideal solution in case of both basic required functions and additional transient tests. This system allows changes in composition of gas as well as of temperature and pressure during the test (i.e. no need to interrupt the test to change conditions).



Picture 6: Block diagram of dynamic testing facility [10]

On the other hand, the facility for such testing is quite complicated, complex and anything but low cost. To demonstrate this, a block representation of such facility is shown above. Another scheme shows practical solution in case of a dynamic system.



Picture 7: Actual schematic representation of dynamic testing facility [11]

The facility is fitted with gas chromatography equipment (GC), controlled evaporation mixer (CEM), mass flow meter (MFM), pressure controllers (PRC), liquid mass flow controller (LMFC) and a number of mass flow controllers (MFC).

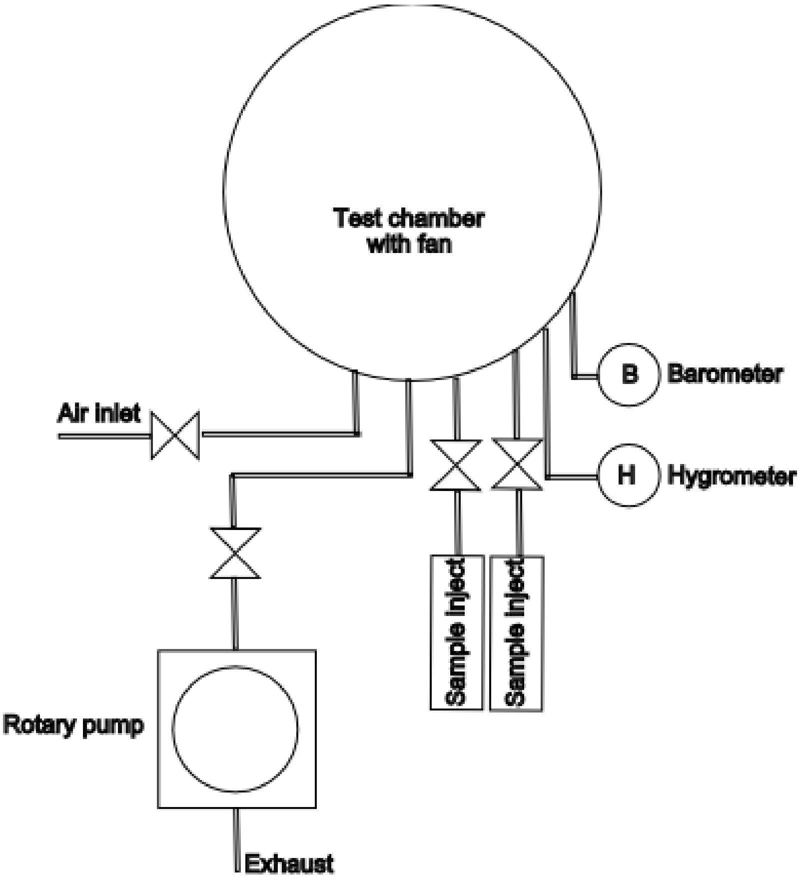
2.1.2. Static system

In case that only static parameters are to be tested, a much easier system can be used. The idea of a static system is that the gas mixture properties do not change during the test. Gas mixture does not flow.

This template was used to design the simple example of a testing facility.

2.1.3. Implementation

The testing facility consists of a chamber of defined volume, rotary pump, hygrometer and barometer (atmospheric conditions in the test chamber) and sample injection devices.



Picture 8: Static facility

To homogenize the mixture, a fan can be installed inside the chamber. Also, thermal sensor can be installed. Rotary pump is connected to enable quick exchange of gas in the chamber to conduct another test.

Sample injection is done by a syringe (also defined amount of gas). The concentration of hydrogen or of other gas (contamination) can then be calculated.

The system can be used for testing various pressures, gas concentrations, humidity and contamination.

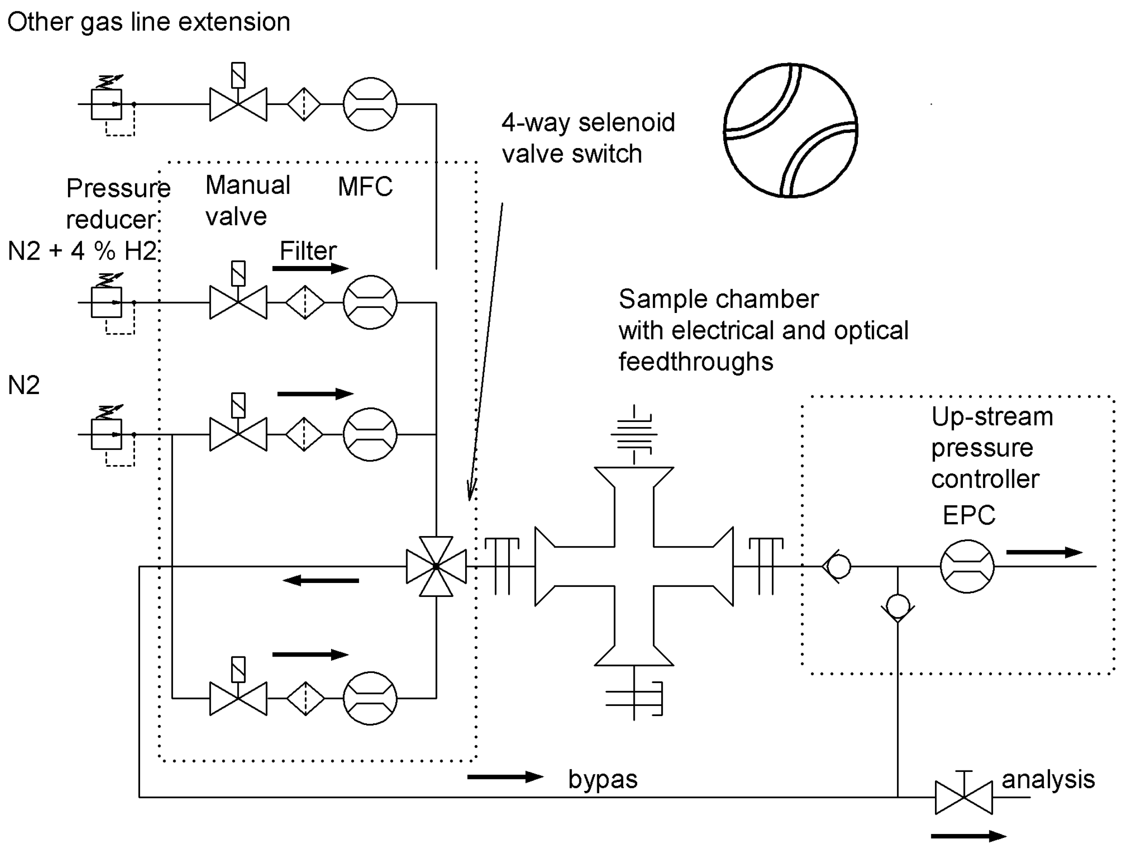
3. Practical solution

3.1. Practical testing

Thanks to Prof. Boušek and Doc. Salyk, the dynamic testing facility of the Faculty of Chemistry was utilized in the measurements. The provided facility is a dynamic facility designed for testing of new experimental sensors designed and manufactured in the laboratory by Doc. Salyk. This project concerns use of new organic materials as sensitive layers in hydrogen sensors.

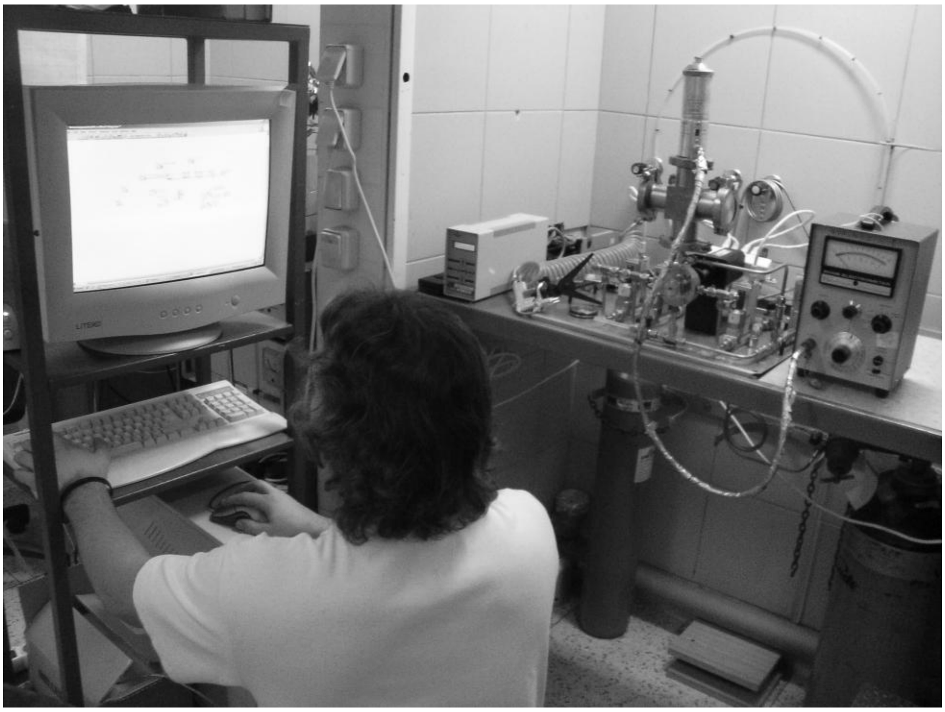
3.1.1. The dynamic facility

As stated above, the provided facility is dynamic. Also it is clear from the provided scheme below.

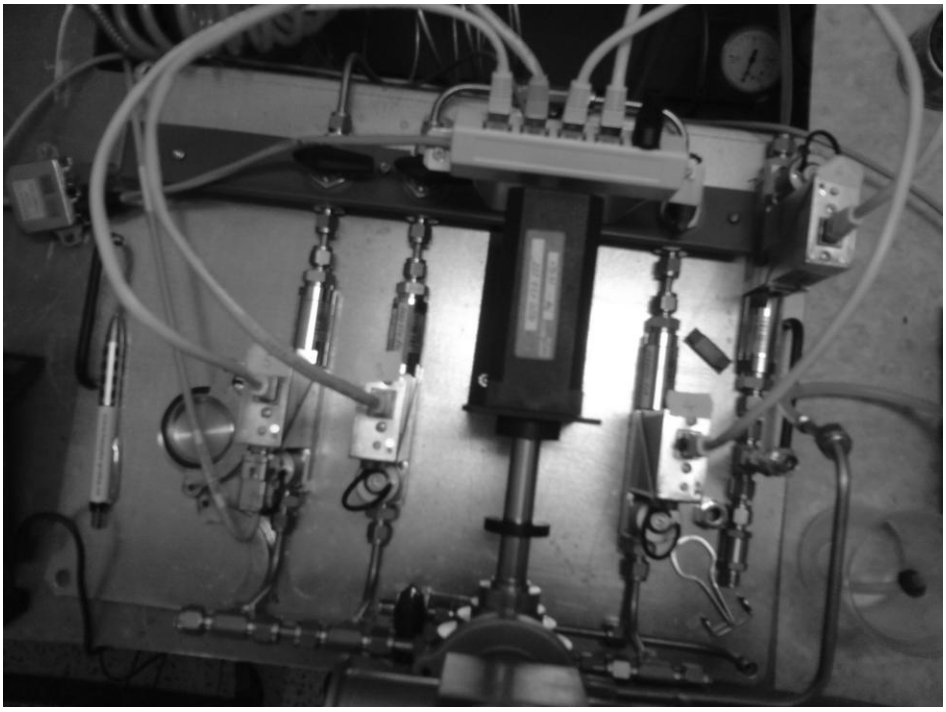


Picture 9: Schematic representation of the provided facility [12]

The facility is mostly automatic, with computer operated mass flow controllers, gas switching and sensor data gathering system. The program is designed using LabView software and exports sensor data to MS Excel. The only operation done manually is switching the range of a battery-operated ampere-meter.



Picture 10: The facility at the Faculty of Chemistry and the control computer [12]



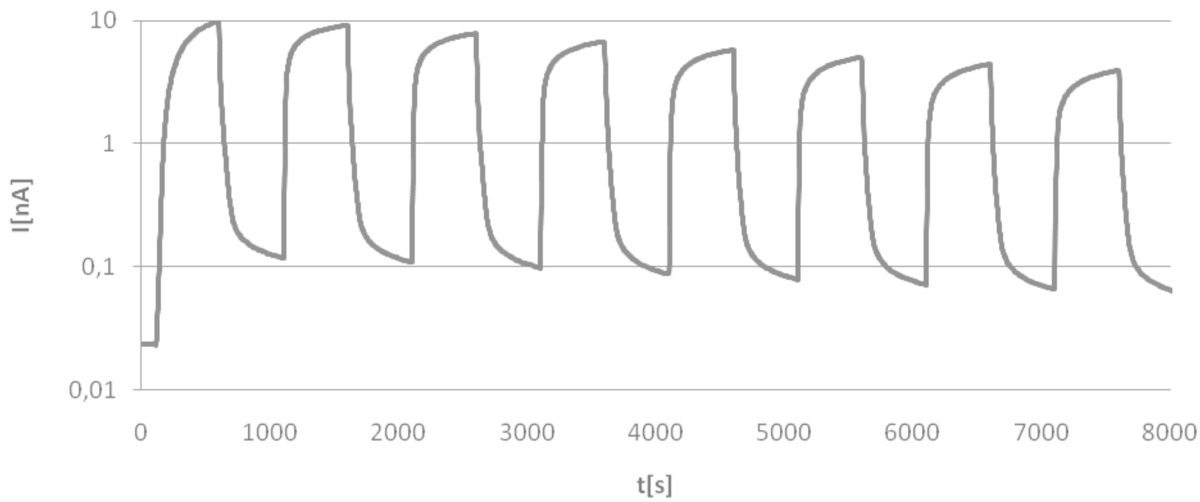
Picture 11: Gas lines with MFCs

The battery operated ampere meter is used to isolate the facility from noise and interference from power lines due to low output currents. Value is then sent to a multi-meter enabling computer connection and from there logged in the program.

Cables are shielded but even so it is a very sensitive facility.

3.1.2 Dynamic mode

As stated in the first part of this paper, the dynamic facility makes repeating of one experiment and consequent degradation observations easier to conclude. The chamber is filled with N_2, sensor output stabilizes, and then the valve is switched to let in mixture of N_2 and H_2. This cycle can be repeated. Sensors equipped with heating element and resistance temperature detector (RTD) allow measurement at higher temperatures. All the measurement is automatic. Only manual work is switching range on ampere meter.



Picture 12: Response of a sensor in dynamic mode

3.1.3. The static facility

The change into a static facility is done by fitting the free feed through with a custom made silicon septum do make sample injection possible by a micro syringe and switching off the line from the gas line extensions.

The chamber volume was measured to later determine concentrations of gasses in the chamber after injection via the septum.

To simulate the function of a static facility, the chamber is filled with air, closed and gas is injected. After output of the sensor stabilizes, the chamber is opened and purged by air to measure the fall time of the sensor.

Also, a gas tank with a valve and a silicon stopper was fabricated and filled with hydrogen to enable drawing of gas into the syringe. Gas tank consists of a three way valve and a water bottle. The advantage of a PET bottle is that it can be easily emptied by squeezing the bottle, so there is no need for pumps or reduction valves for changing of content.

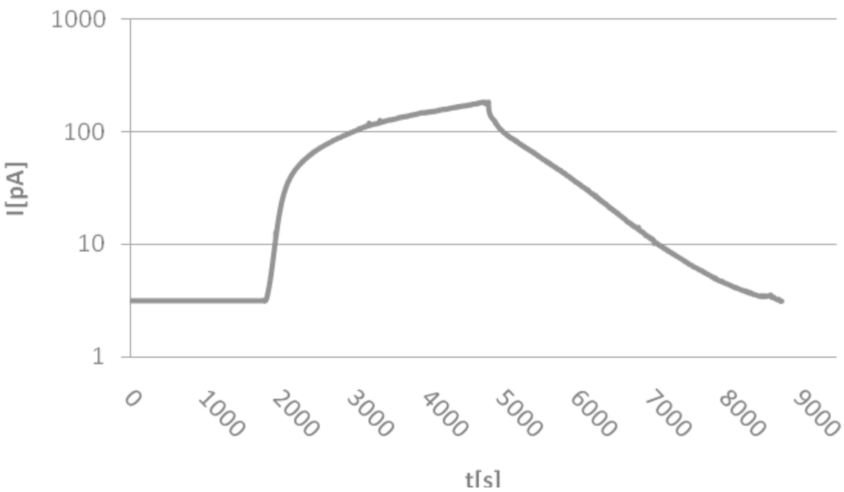
Picture 13: Gas tank

3.1.4 Static mode

The measurement in static mode was concluded the way described above. A mixture containing 1% of H_2 was obtained in the chamber after injection. Stabilization at the beginning of test was observed by the operator. When the system was considered stabilized, testing started. Again, when the output was considered stable, the chamber was opened and purged. It can be seen that the test took longer to conduct in static mode than in dynamic mode.

Nothing except for the output measurement and logging was done automatically. Degradation cannot be observed in one test alone.

The advantage of this method is the possibility to achieve very low concentrations of gasses in the chamber.



Picture 14: Response in static mode

4. Sensors

4.1. Pyridine sensors

4.1.1. Sensor platform

These sensors are fabricated on corundum sensor platforms manufactured by Tesla Blatná, a.s.

Sensor platform specifications

Temperature range

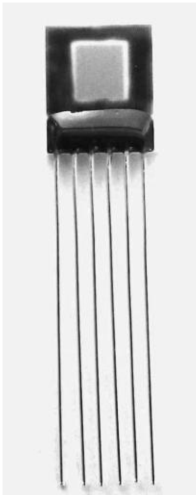
-50°C to 450°C

Temperature sensor

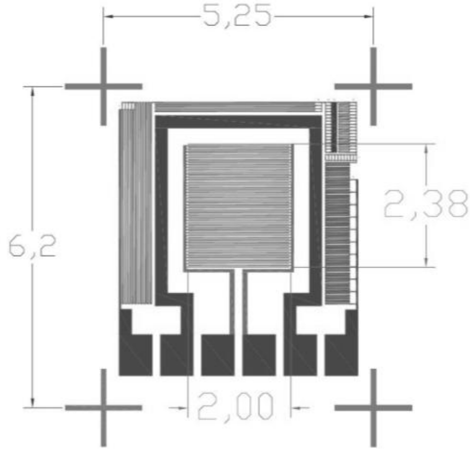
1000 Ohm for 0°C, 2B class

Heater

3W power output for 450°C



Picture 15: Sensor platform



Picture 16: Platform dimensions

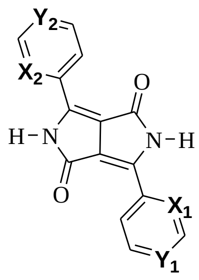
4.1.2. Sensitive material

The common short name of the family of analogue compounds is diketopyrrolopyrrole abbreviated as DPP.

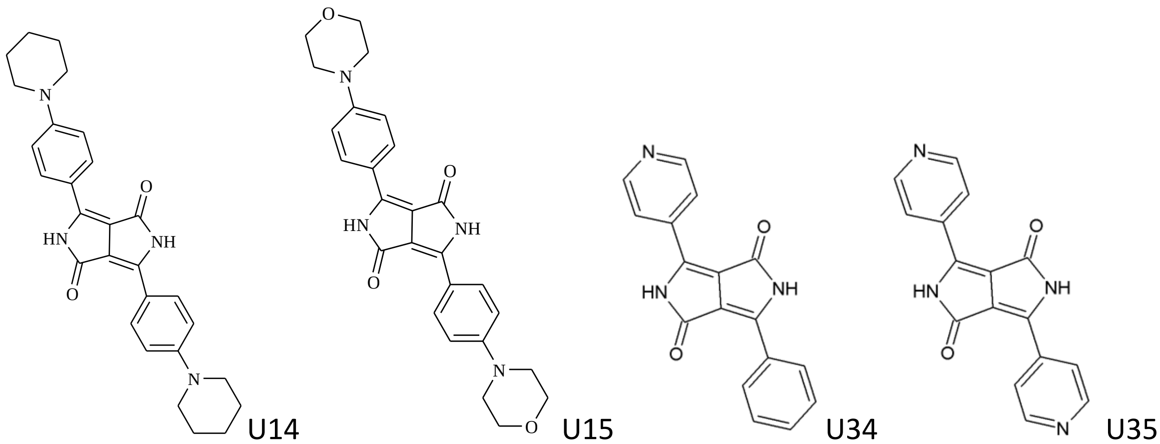
Sensitive layer of these sensors consists of DPP and palladium. Some sensors are also covered by a melamine layer to determine its potential as a barrier.

Used DPPs are commonly used in industry as red pigments. These are therefore cheap and widely available.

Melamine is also a common base for barrier layers due to its geometry. Melamine molecules create a honeycomb structure on the surface. The idea is that melamine is to prevent larger molecules (such as oxygen) to get to the surface of active layer.

	BPPB	X_1=X_2=Y_1=Y_2=CH
	2PyPPB	X_1=N, X_2=Y_1=Y_2=CH
	2PyPP2Py	X_1= X_2=N, Y_1=Y_2=CH
	4PyPPB	X_1=X_2 = CH, Y_1= N, Y_2=CH
	4PyPP4Py **(DPPP)**	**X_1**= **X_2**=CH, **Y_1**=**Y_2**=N

Picture 17: 4PyPP4Py or 3,6-bis-(4´-Pyridyl)-2,5-Dihydro-Pyrrolo[3,4-C]Pyrrole-1,4-Dione (DPPP - DiPyridyl-diketoPyrrolo-Pyrrole) and the family of some DPP analogues [13]



Picture 18: Used DPPs with code

Sample name consists of a material code and fabrication date. It can be complemented with a remark. Change of resistivity is observed on sensors with these materials as sensitive layers.

5. Strategy of Measurement

5.1. Standard measurement procedure

The need for a standard procedure exists for evaluation purposes. It is then possible to overlap results of various setups in one graph making the differences obvious.

The standard testing procedure was set to five exposures to hydrogen for 500 seconds and consequent purging of the facility with air or nitrogen for 500 seconds.

Initially, the facility is purged by air or nitrogen. Sensor output is observed. After sensor output stabilizes, standard testing procedure is started.

At the end of the procedure, the facility is purged for long period of time (tens of minutes to hours depending on sample type) to determine time constant of the sensor.

It is also possible to heat the sample from laboratory temperature up to temperatures of destruction of the sample. The destruction of sample is usually due to evaporating of the sensing layer. The sample is heated by the heater on the sensor pad. Some sensors do not have heaters. For heating of these sensors it is needed to heat the chamber and observe temperature inside.

5.2. Measurement variations

Most important parameters of the sensor are sensitivity, response time and cross-sensitivity. Also, sensor recovery is an issue, since some sensors have proven sensitivity to hydrogen, but responded to purging insufficiently.

Sensitivity of this specific sensor can be in the increased by heating the pad. The process of heating the facility and temperature stability is strongly affected by power supply stability.

If sensor is not equipped with a heating pad, the whole facility can be heated. In these cases however, the temperature cannot be set precisely.

During fabrication, two identical sensors are made in each batch enabling further observations of the effect of aging and regeneration of the sensors. Further changes of one sensor and consequent comparison of results is made possible. Also, it has proven advisable to conclude more measurements during longer periods of time, since some sensors tend to degenerate rapidly.

6. Testing

6.1. Organic sensors

As stated above, different materials were deposited on the sensor platform. U14, U34, U35 U54 and U57 were tested. The test goal was to determine the suitable material for sensitive layers of hydrogen sensors.

Sensitivity, response time, cross-sensitivity, linearity, stability in time and reversibility are the parameters that have to be determined for such applications. In below stated tests, these parameters were determined, except cross-sensitivity.

U35 sensor displayed most promising results, and is therefore investigated in this work. Also, most extensive testing was conducted with this material.

The material is deposited by evaporation in the Faculty of Chemistry laboratory by doc. Ota Salyk. Two sensors are fabricated in every batch.

6.1.1. Effect of degradation

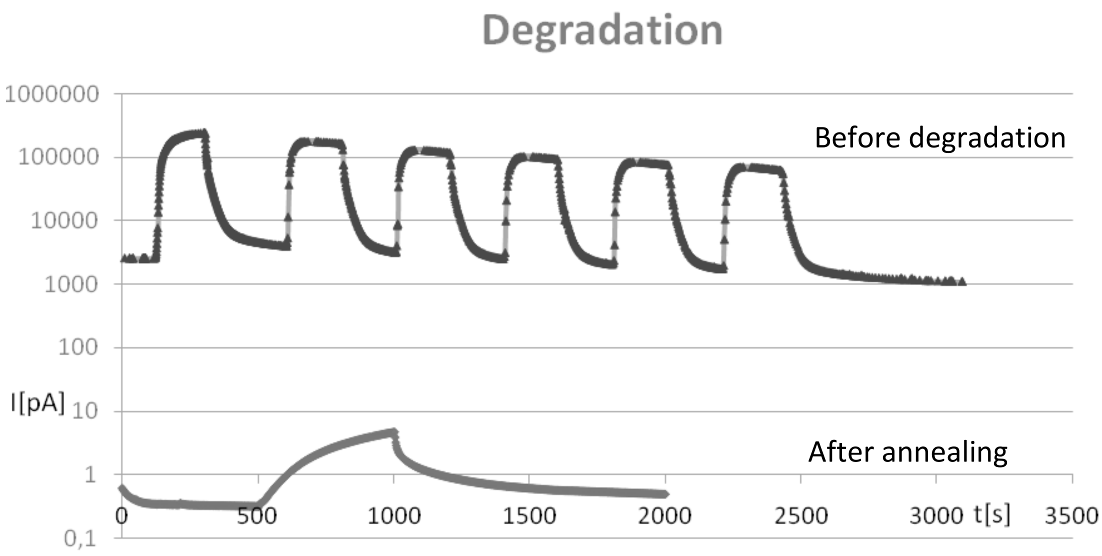
This sample has been let to degrade. Consequently, the sample was annealed in vacuum in order to restore it. Loss of sensitivity is anticipated after the degradation.

Test conditions

Sample**:** U35C-230210

Supply voltage: 2VBefore degradation – response to 5% H_2/N_2, purged by air

After annealing – response to 1% H_2/N_2, purged by air



Picture 19: Effect of degradation

It is apparent, that the sample has lost its sensitivity due to degradation of the sample over time. Annealing of the sample did not improve this feature. Also, degradation of response can be observed during the test. Cause of output drop was not sufficiently explained yet.

6.1.2. Effect of different carrier and purge gasses

This test was concluded in order to determine effects of nitrogen or air usage for purging and as carrier gas. The main concern is the presence of oxygen, which has proven to affect the response negatively.

Loss of sensitivity due to exposure to oxygen is expected. Also, it is expected that purging by air will prove more effective.

Test conditions

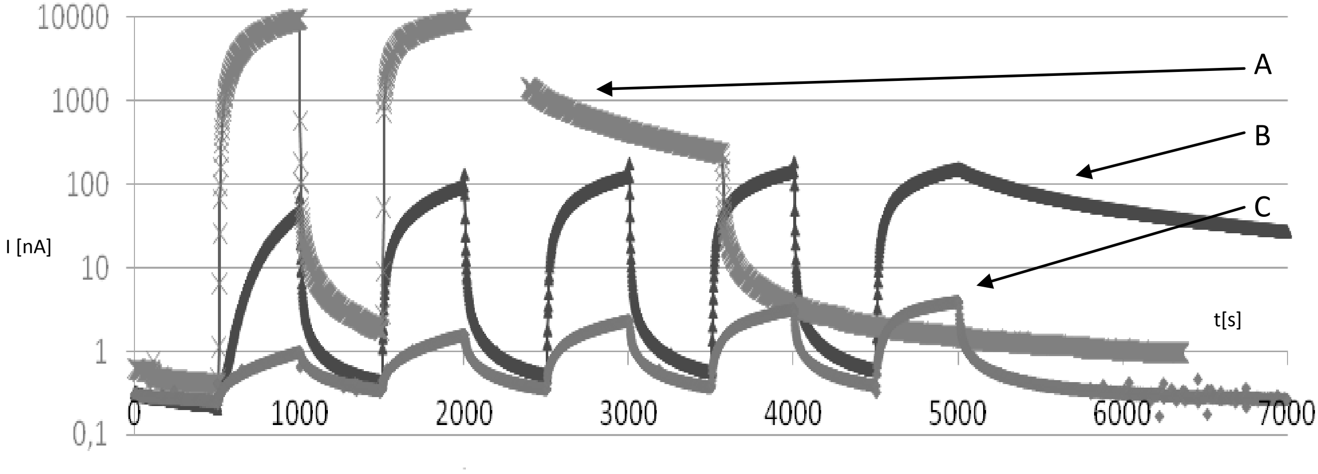
Sample: U35-140610

Supply voltage: 2V

A - Temperature - 80°C, 1% H_2/N_2, first purge by air, second purge by N_2, at 3500s changed to air

B - Temperature - room temperature, 1% H_2/N_2, purge by air, last purge by N_2

C - Temperature - room temperature, 1% H_2/air, purge by air



Picture 20: Effect of different carrier and purge gasses

It is evident from this test that presence of oxygen affects the response (lowers it) and the regeneration of sensor (faster regeneration in air). It is therefore assumed, that atmospheric O_2 blocks bonding of H_2 to the DPP.

6.1.3. Effect of melamine layer

This test is executed in order to determine effect of melamine layer on response to H_2. Since it is known that oxygen has a negative effect on sensitivity, the test is to prove possibility of using melamine as a barrier layer to prevent oxygen from reaching the surface of the active layer.

Test conditions

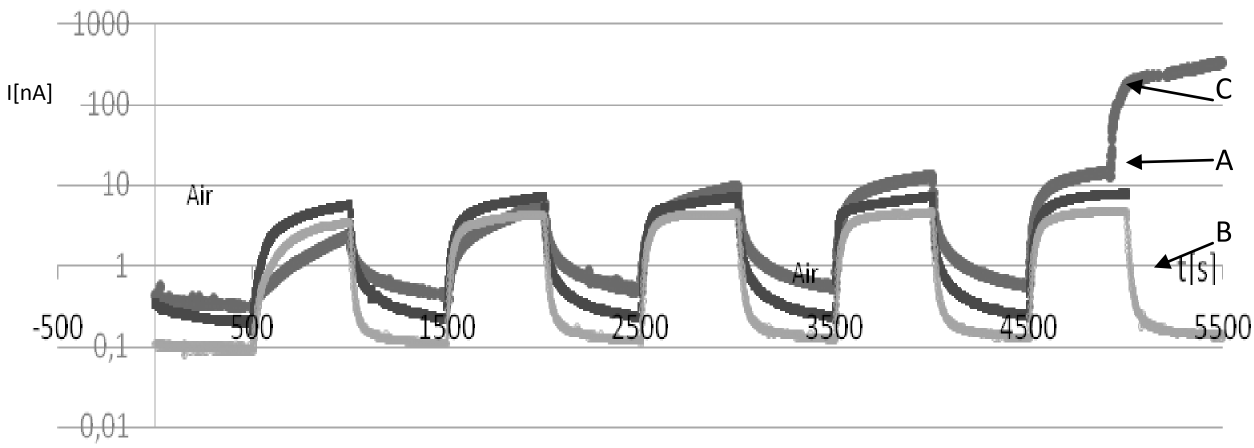
Sample: U35-140610

Supply voltage: 2V

100nm (A), 200nm (B) and 1000nm (C) melamine layer

Room temperature

Response to 1%H_2/air, purge by air



Picture 21: Effect of melamine layer

It is evident from the results that melamine has minimum effect on the response. This shows the idea of melamine as a barrier layer ineffective.

Alternatively, it may point to the fact, that due to granular structure of DPP layer, melamine layer is not uniformly formed on the surface.

6.1.4. Temperature changes and effects

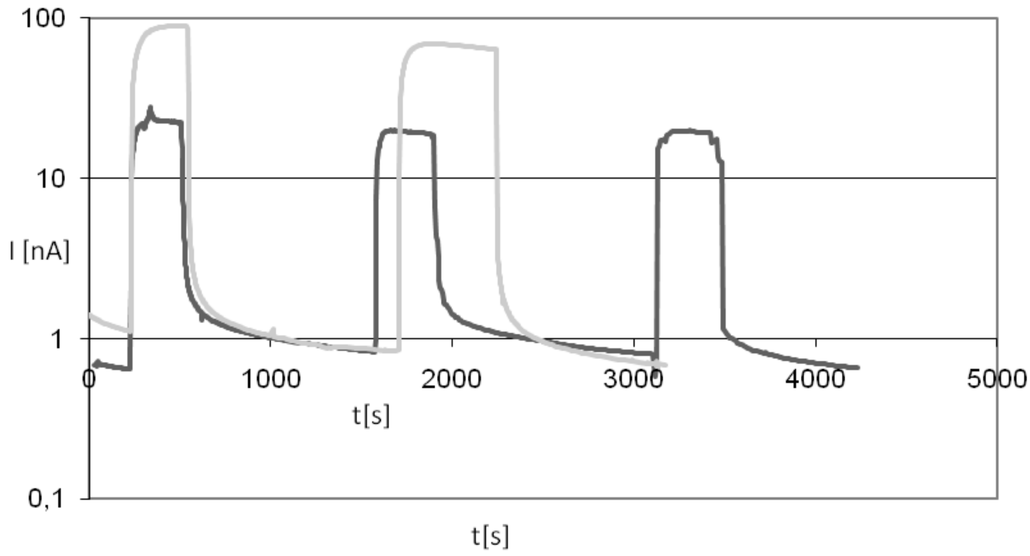
This test was set up to determine temperature dependency of the response. It is expected that higher temperatures lift also the response current in the sensor due to higher reaction rate on the sensor surface.

Test conditions

Sample: U35C-230210

Response to 5%H_2/N_2, purged by air

Temperatures – room temperature and 80°C



Picture 22: Effect of temperature on response

It is obvious that temperature has a significant effect on the response. The output signal rises with temperature. This is happening probably due to increased reaction rate under higher temperatures.

6.1.4. Volt-Ampere characteristics

Volt-Ampere characteristics were measured in order to determine the effect of different supply voltages on the sensor output.

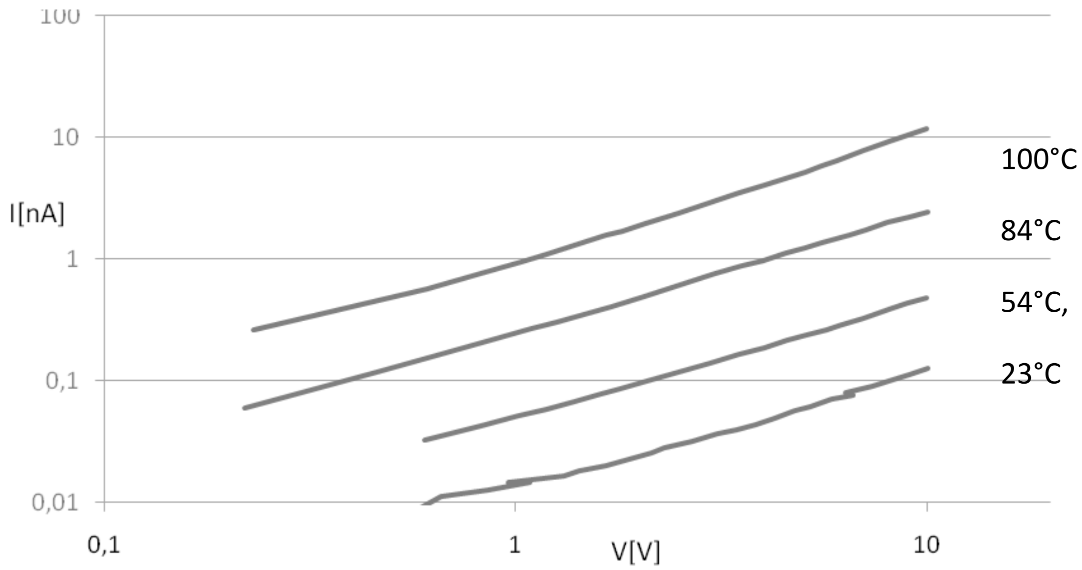
Test conditions

Sample: U35C-230210

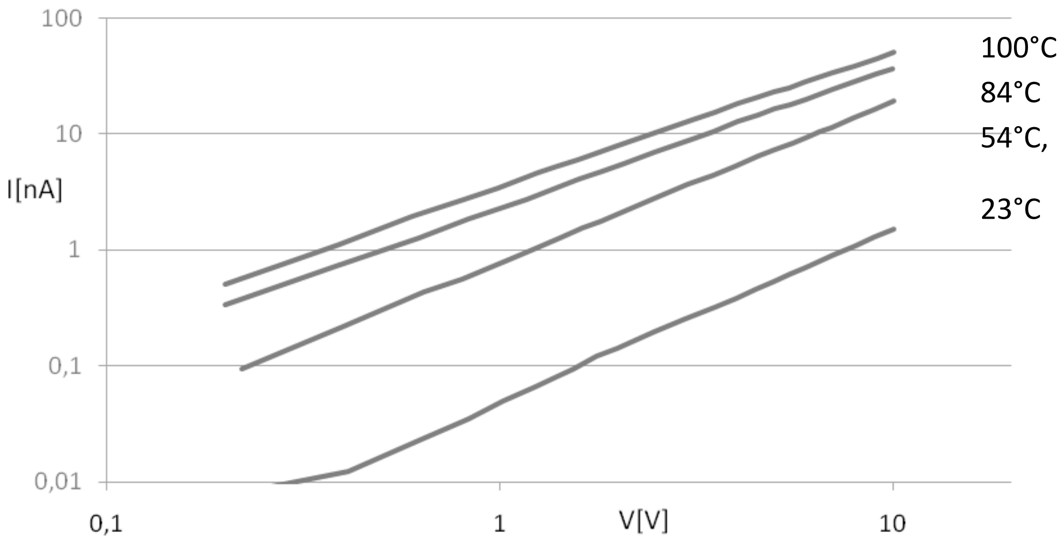
Voltage range 0 to 10V

In air without H_2 and 1% H_2 in air

Temperatures: 23°C, 54°C, 84°C and 100°C



Picture 23: Volt-Ampere characteristics of sensor in air without H_2



Picture 24: Volt-Ampere characteristics of sensor in 1% H_2 in air

Volt-Ampere characteristics of sensor are approximately linear. Also, it can be observed that in H_2 the effect of temperature is less significant. Furthermore, a contact barrier can be observed at low voltages.

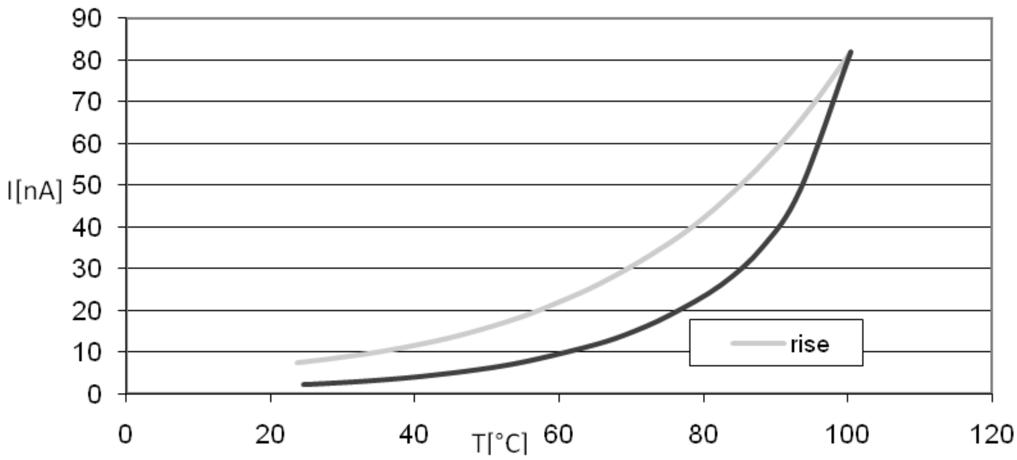
6.2. Temperature fluctuation

Temperature fluctuation can affect output of sensors. Further study of the effects is vital to accurate sensor testing.

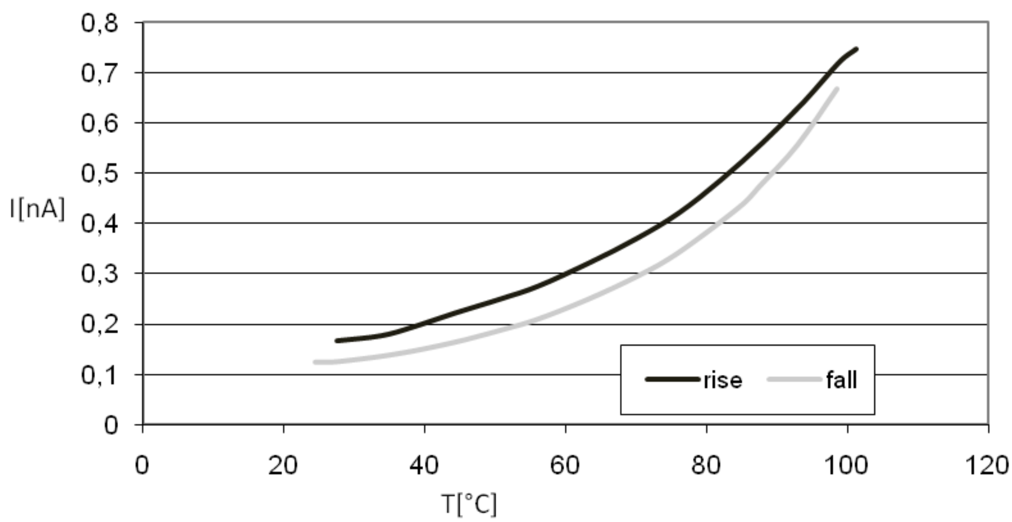
6.2.1 Temperature fluctuation effects

As seen in the previous test, temperature changes have a significant effect on the sensor output. This leads to the need to control and stabilize temperature precisely. Temperature setting was done by connecting 1.5V cells to the heater. More cells were connected in series to provide higher voltage and therefore higher temperature.

It is necessary to determine the dependence of output current, resp. sensor resistance on temperature of sensor platform. As shown above, a significant effect can be anticipated.



Picture 25: Effect of temperature on sensor in 1% H_2



Picture 26: Effect of temperature on sensor in air

These graphs clearly show the dependence of sensor current on temperature. The characteristics are not linear. Furthermore, rising slope and falling slope characteristics vary. Extrapolation of results may be difficult due to this fact. This leads to the need for a temperature stabilization during testing to ensure that observed effects are caused by sensor, not by fluctuating temperature.

As seen from above, temperature fluctuation is a serious issue in case of organic sensor testing due to higher reactivity of sensing layer under higher temperatures.

6.2.2. Temperature fluctuation causes

Causes of temperature fluctuation can be found in source for heating element on the sensor platform.

Initially, 1.5V, respectively 1.2V rechargeable cells were used to heat the platform limiting the temperature setting to levels reachable by a fixed voltage. Serial connection of cells was also possible to obtain higher voltage.

However, this approach has proven unreliable since the cells tended to discharge and therefore the heating element would not supply sufficient heat to maintain temperature and the sensor would cool down.

Later, cells were replaced by a stabilized laboratory voltage source. The voltage source was able to maintain stable voltage. But the manual setting has proven unreliable as well since the temperature took long to stabilize and would eventually drift due to long temperature stabilization time.

Also, connecting of an Ohm-meter to the Pt1000 RTD sensor caused serious interference in the measurement setup, making continuous temperature monitoring impossible.

The need for a stable, temperature-regulated source for the heater arose from these drawbacks.

7. Regulator design

7.1. Motivation

The need to be able to measure sensors under stable temperature has been the motivation for this design. Stable conditions are essential to determine behavior of the sensor. Also, determining voltage drops has been difficult since it was impossible to have the Ohm-meter connected throughout the measurement due to interference.

7.2. Specifications

Requirements:

- Temperature range up to 200°C
- Interference suppression
- Usable for KBI2 sensor platform by Tesla Blatná
- Stabilized laboratory DC source
- Adjustable temperature

7.2.1. Pt1000 resistance thermometer

Platinum resistance thermometers offer excellent accuracy over a wide temperature range (from -200 to +850 °C). Standard sensors are available from many manufacturers with various accuracy specifications and numerous packaging options to suit most applications. Unlike thermocouples, it is not necessary to use special cables to connect to the sensor.

The principle of operation is to measure the resistance of a platinum element. The most common type (Pt100) has a resistance of 100 ohms at 0 °C and 138.4 ohms at 100 °C. There are also Pt1000 sensors that have a resistance of 1000 ohms at 0 °C. [14]

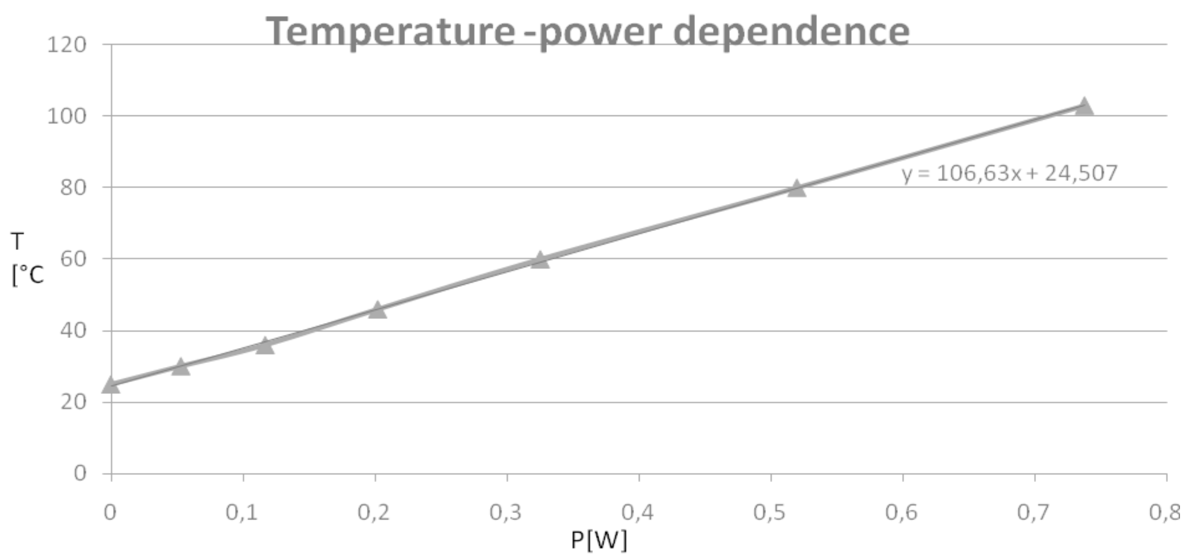
°C	0	1	2	3	4	5	6	7	8	9
0	1000,0	1003,9	1007,8	1011,7	1015,6	1019,5	1023,4	1027,3	1031,2	1035,1
10	1039,0	1042,9	1046,8	1050,7	1054,6	1058,5	1062,4	1066,3	1070,2	1074,0
20	1077,9	1081,8	1085,7	1089,6	1093,5	1097,3	1101,2	1105,1	1109,0	1112,9
30	1116,7	1120,6	1124,5	1128,3	1132,2	1136,1	1140,0	1143,8	1147,7	1151,5
40	1155,4	1159,3	1163,1	1167,0	1170,8	1174,7	1178,6	1182,4	1186,3	1190,1
50	1194,0	1197,8	1201,7	1205,5	1209,4	1213,2	1217,1	1220,9	1224,7	1228,6
60	1232,4	1236,3	1240,1	1243,9	1247,8	1251,6	1255,4	1259,3	1263,1	1266,9
70	1270,8	1274,6	1278,4	1282,2	1286,1	1289,9	1293,7	1297,5	1301,3	1305,2
80	1309,0	1312,8	1316,6	1320,4	1324,2	1328,0	1331,8	1335,7	1339,5	1343,3
90	1347,1	1350,9	1354,7	1358,5	1362,3	1366,1	1369,9	1373,7	1377,5	1381,3
100	1385,1	1388,8	1392,6	1396,4	1400,2	1404,0	1407,8	1411,6	1415,4	1419,1
110	1422,9	1426,7	1430,5	1434,3	1438,0	1441,8	1445,6	1449,4	1453,1	1456,9
120	1460,7	1464,4	1468,2	1472,0	1475,7	1479,5	1483,3	1487,0	1490,8	1494,6
130	1498,3	1502,1	1505,8	1509,6	1513,3	1517,1	1520,8	1524,6	1528,3	1532,1
140	1535,8	1539,6	1543,3	1547,1	1550,8	1554,6	1558,3	1562,0	1565,8	1569,5
150	1573,3	1577,0	1580,7	1584,5	1588,2	1591,9	1595,6	1599,4	1603,1	1606,8
160	1610,5	1614,3	1618,0	1621,7	1625,4	1629,1	1632,9	1636,6	1640,3	1644,0
170	1647,7	1651,4	1655,1	1658,9	1662,6	1666,3	1670,0	1673,7	1677,4	1681,1
180	1684,8	1688,5	1692,2	1695,9	1699,6	1703,3	1707,0	1710,7	1714,3	1718,0
190	1721,7	1725,4	1729,1	1732,8	1736,5	1740,2	1743,8	1747,5	1751,2	1754,9
200	1758,6	1762,2	1765,9	1769,6	1773,3	1776,9	1780,6	1784,3	1787,9	1791,6
210	1795,3	1798,9	1802,6	1806,3	1809,9	1813,6	1817,2	1820,9	1824,6	1828,2
220	1831,9	1835,5	1839,2	1842,8	1846,5	1850,1	1853,8	1857,4	1861,1	1864,7
230	1868,4	1872,0	1875,6	1879,3	1882,9	1886,6	1890,2	1893,8	1897,5	1901,1
240	1904,7	1908,4	1912,0	1915,6	1919,2	1922,9	1926,5	1930,1	1933,7	1937,4
250	1941,0	1944,6	1948,2	1951,8	1955,5	1959,1	1962,7	1966,3	1969,9	1973,5
260	1977,1	1980,7	1984,3	1987,9	1991,5	1995,1	1998,7	2002,3	2005,9	2009,5
270	2013,1	2016,7	2020,3	2023,9	2027,5	2031,1	2034,7	2038,3	2041,9	2045,5
280	2049,0	2052,6	2056,2	2059,8	2063,4	2067,0	2070,5	2074,1	2077,7	2081,3
290	2084,8	2088,4	2092,0	2095,6	2099,1	2102,7	2106,3	2109,8	2113,4	2117,0
300	2120,5	2124,1	2127,6	2131,2	2134,8	2138,3	2141,9	2145,4	2149,0	2152,5
310	2156,1	2159,6	2163,2	2166,7	2170,3	2173,8	2177,4	2180,9	2184,4	2188,0
320	2191,5	2195,1	2198,6	2202,1	2205,7	2209,2	2212,7	2216,3	2219,8	2223,3
330	2226,8	2230,4	2233,9	2237,4	2240,9	2244,5	2248,0	2251,5	2255,0	2258,5
340	2262,1	2265,6	2269,1	2272,6	2276,1	2279,6	2283,1	2286,6	2290,2	2293,7
350	2297,2	2300,7	2304,2	2307,7	2311,2	2314,7	2318,2	2321,7	2325,2	2328,7
360	2332,1	2335,6	2339,1	2342,6	2346,1	2349,6	2353,1	2356,6	2360,0	2363,5
370	2367,0	2370,5	2374,0	2377,4	2380,9	2384,4	2387,9	2391,3	2394,8	2398,3
380	2401,8	2405,2	2408,7	2412,2	2415,6	2419,1	2422,6	2426,0	2429,5	2432,9
390	2436,4	2439,9	2443,3	2446,8	2450,2	2453,7	2457,1	2460,6	2464,0	2467,5
400	2470,9	2474,4	2477,8	2481,3	2484,7	2488,1	2491,6	2495,0	2498,5	2501,9

Table 1: Pt1000 resistivity table

7.2.2. Sensor platform heating element test

Sensor platform manufacturer states, that maximum output thermal power of sensor platform heater is 3W at 450°C. However, it was necessary to determine, if the characteristic is linear. This feature is not evident from the sensor platform datasheet.

Using a stable laboratory source, temperature dependence on supplied power was plotted.



Picture 27: Temperature-power dependence

From the performed test of sensor platform it is obvious that the temperature is linearly dependent on the supplied power.

7.3. Design

7.3.1. Temperature regulation circuit

This design was made to enable setting of temperature, and temperature stabilization of heater resistor.

7.3.1. Core circuit

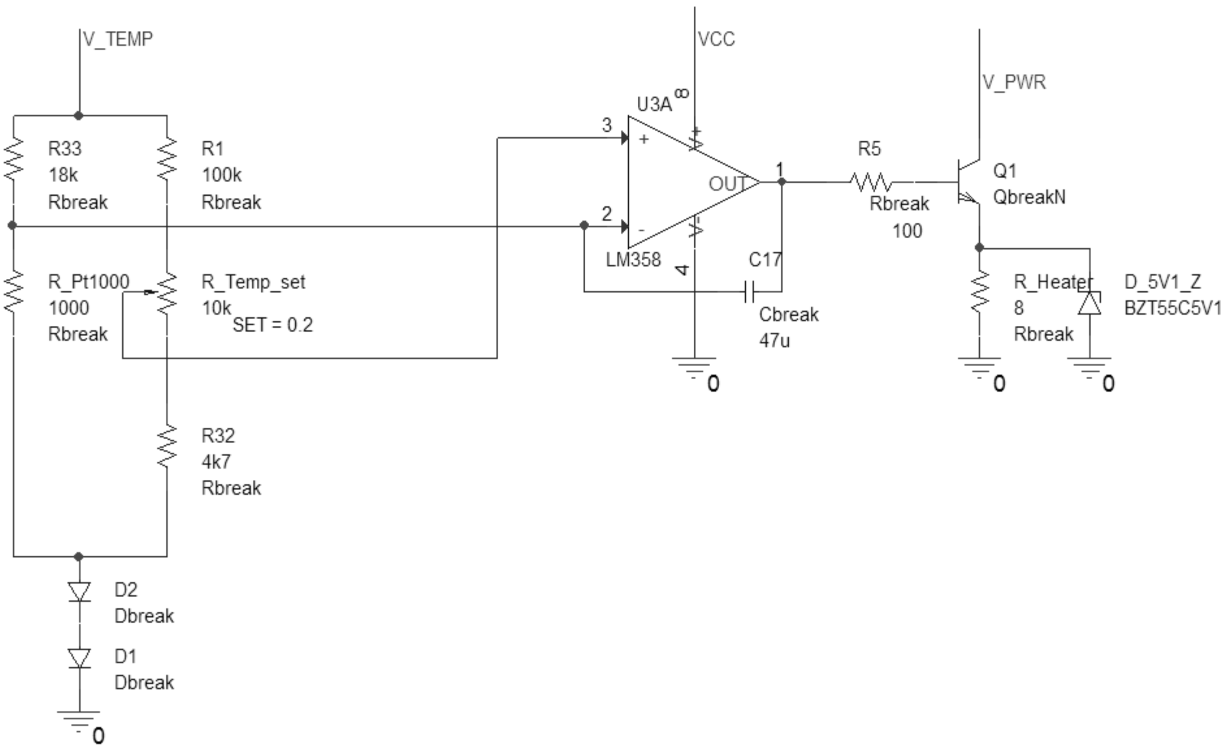
The circuit is based on the idea of a balanced bridge, where disbalance is created by difference between set temperature and temperature of the heater resistor.

Operational amplifier is used to determine if the heating is necessary. It is essential to understand that the heater and the Pt 1000 temperature sensor are on the same platform therefore creating a non-electric negative feedback.

Description

5V stabilized V_TEMP voltage is connected to the bridge. Two voltage dividers are present in this circuit, one with the Pt1000 RTD, and the other with a setting potentiometer. These determine operation of the operational amplifier. Two diodes are used to raise voltage on the bridge connection nodes due to the fact, that the operational amplifier has asymmetrical supply and therefore is not able to determine low voltage differences. The operational amplifier also has a negative feedback loop through a capacitor to prevent oscillation.

Bipolar transistor is connected to the operational amplifier by base. This has to be a power transistor since the peak currents can reach over 500mA. The collector is connected to 5V stabilized V_PWR voltage. Emitter of the bipolar transistor is connected to the heater of the sensor platform. Parallel to the heater, a 5.1V Zener diode is connected for safety purposes.



Picture 28: Circuit core schematic

Function

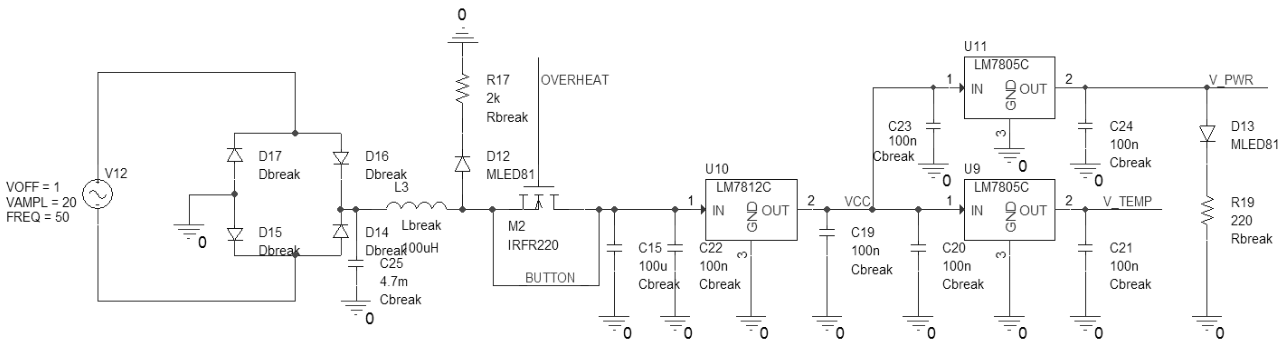
Voltage difference is created when Pt1000 RTD has different voltage than the one set by setting potentiometer. This is due to different temperature of the sensor platform than desired.

In case temperature is low, the operational amplifier output is 12V opening the bipolar transistor. This leads to temperature rise.

In case temperature is high, the operational amplifier output is 0V closing the bipolar transistor. This leads to temperature drop.

In case of transistor failure the Zener diode protects the heater from overvoltage.

7.3.3. Supply subcircuit



Picture 29: Supply subcircuit schematic

Description

5V and 12V supply voltages were chosen for this application. The operational amplifiers have asymmetrical supply from a 12V LM7812 stabilizer (VCC net). This stabilizer provides supply for two 5V LM7805 stabilizers. These are independent power and measurement sources (V_PWR and V_MEAS). Since V_MEAS source supplies the measurement bridge and one voltage divider, it is possible to use a LM78L05, which has output current limited to 100mA. This is not possible for V_PWR, since output current required from this stabilizer can be significantly higher due to the heater connected to this stabilizer.

Function

To make AC voltage supply usable and also to prevent operator errors, the first part of the supply subcircuit is a Graetz rectifier. It is followed by a filter capacitor and a choke coil. At this node, a LED indicator is connected to signalize connection to a power source. The LED is powered independently on the failsafe mentioned lower.

MOS transistor acts as a safety switch. Its gate is operated by an overheating monitoring circuit. In case of overheating, the whole circuit is shut down.

The MOS transistor opens when voltage is supplied to the gate. Monitoring circuit supplies 12V to the gate in case of normal operation. In case of error, the voltage drops to 0V and shuts the whole circuit down preventing sensor damage. This operation was selected due to the fact, that reverse operation would not have desired effect, since the circuit would automatically start again resulting in oscillation of the whole circuit. In the current setup, after supply voltage is provided, the MOS has to be bypassed by a button switch to start operation.

By the above mentioned setup, a LM7812 stabilizer and two LM7805 stabilizers are supplied, providing 12V VCC supply voltage for operational amplifiers and 5V V_TEMP and V_PWR voltages for circuit operation.

Also, a LED is connected to V_PWR indicating, that the whole regulator circuit is operational.

7.3.4. Failsafe mechanisms

To protect the circuit from operator error and failure of parts, failsafe mechanisms are implemented to the design.

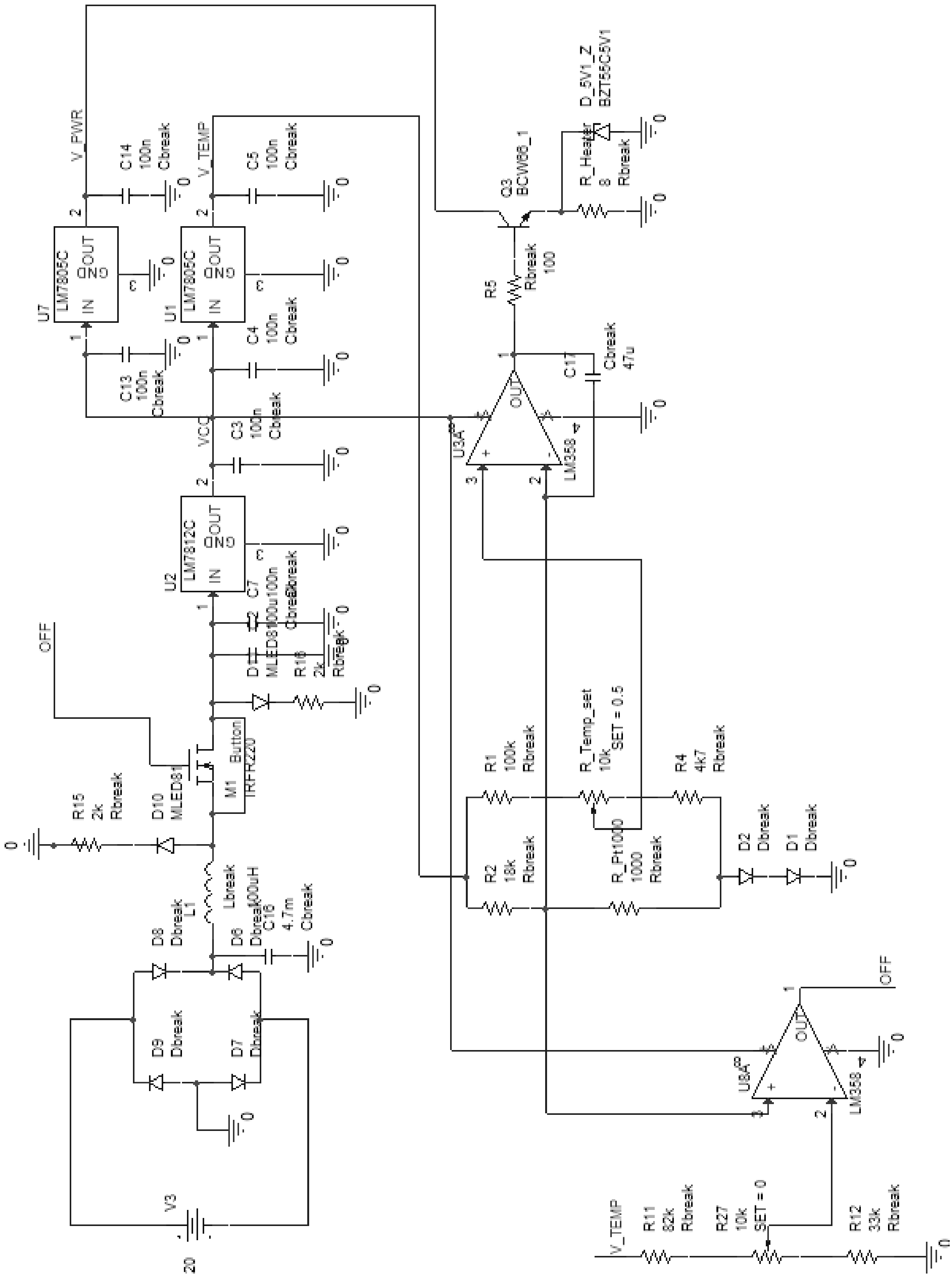
A Graetz bridge rectifier was added to prevent circuit damage in case of AC voltage supply.

R_Heater heating element is protected from circuit failure by a 5.1V Zener diode.

A comparator was added to control possible overheating of the platform. Inputs of this comparator are: a divider node with variable voltage level set by a potentiometer and a node of the bridge, where the Pt1000 is connected. Since the comparator has nonsymmetrical supply, the diodes were needed to raise voltage of the Pt1000 node.

Comparator is connected to gate of the MOS transistor. The MOS transistor gate is at 11V level in normal operation. In case of overheat; the comparator output will drop to 0V closing the transistor. This MOS transistor controls power supply of the whole circuit.

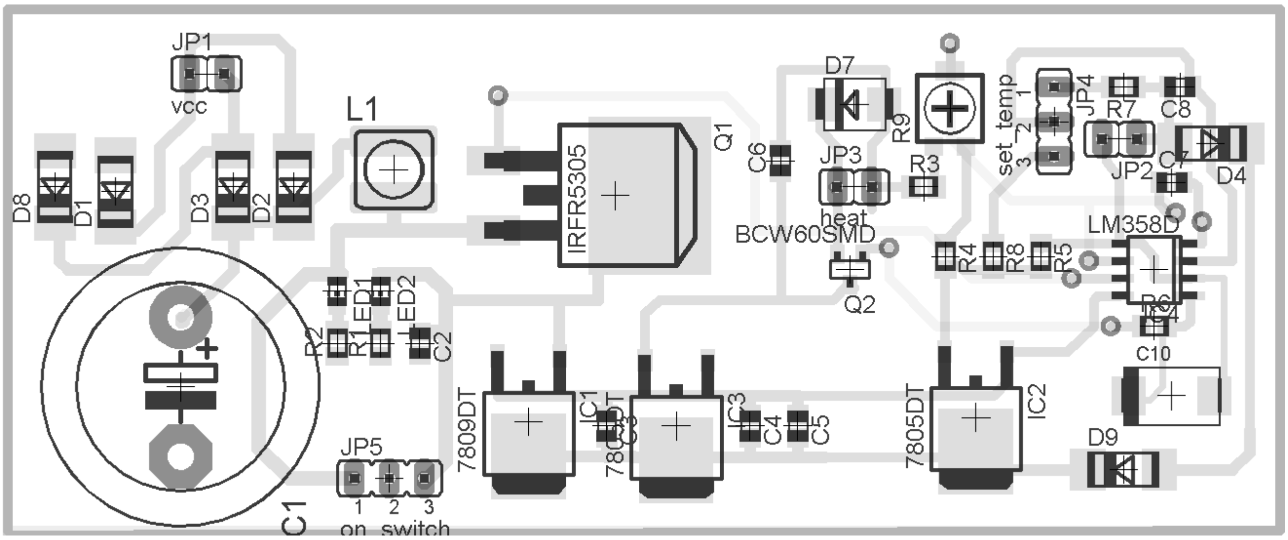
Emergency shutdown temperature can be set by the comparator potentiometer to enable custom setting for different materials.



Picture 30: Circuit schematic

7.3.5. Printed circuit board design

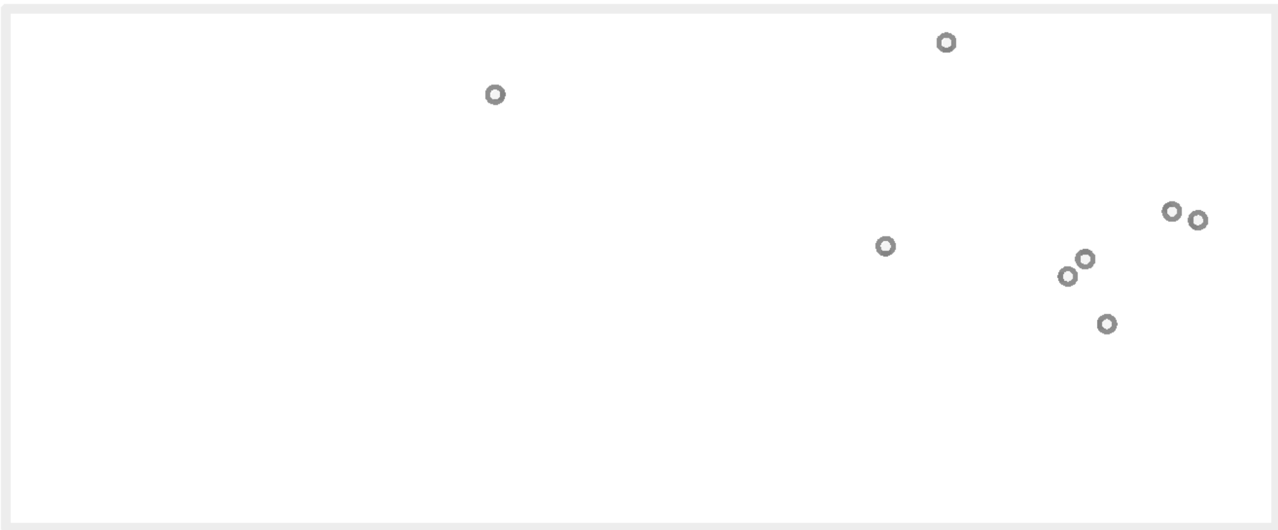
The printed circuit board is designed in Eagle Layout Editor. Jumpers JP2 and JP3 serve as connections to the sensor platform, Pt1000 and heating element connections respectively. Jumper JP4 serves as a connection node for the potentiometer R_Temp_Set.



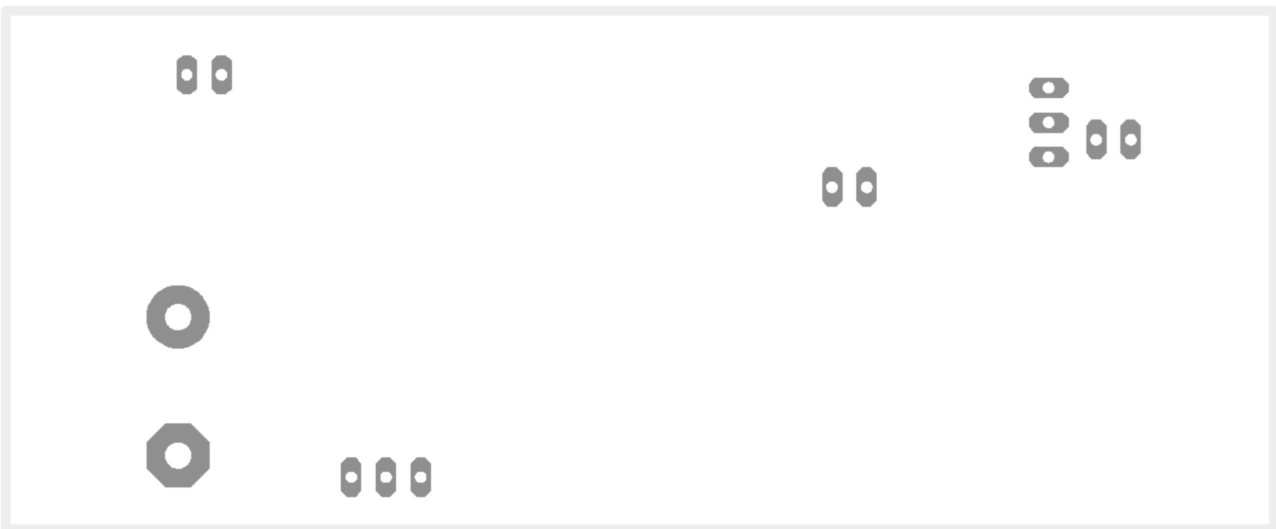
Picture 31: PCB layout – all parts and connections

Picture 32: PCB layout – top side

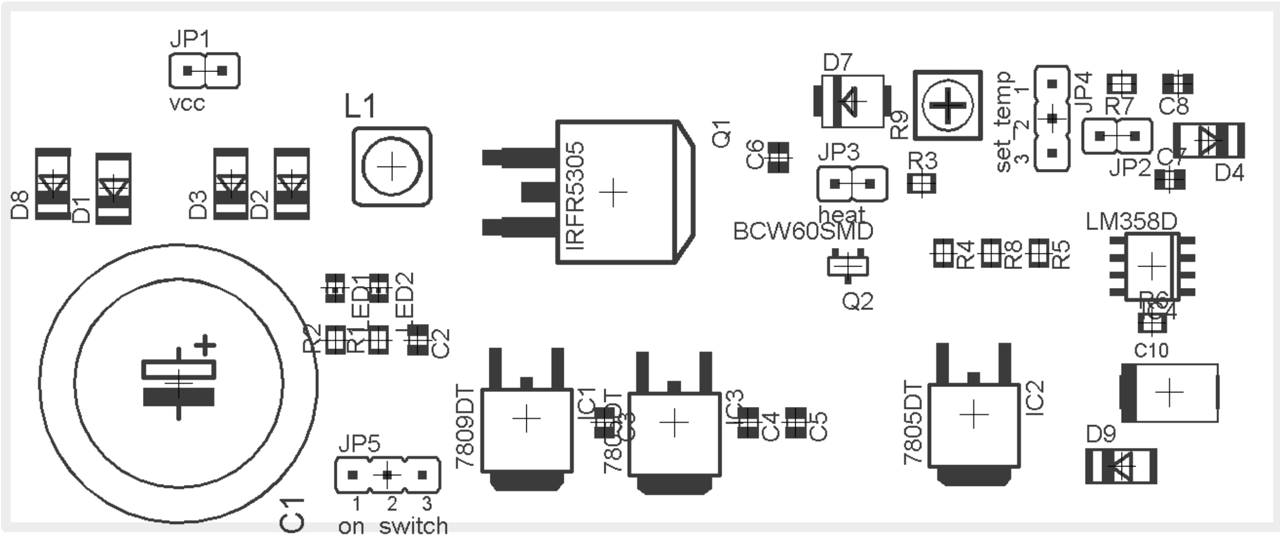
Picture 33: PCB layout – bottom side



Picture 34: PCB layout – vias



Picture 35: PCB layout – solder pads for THT parts



Picture 36: PCB layout – part placement

7.3.6. Part selection

Part	Model	Package	Quantit
R_Temp_Set	PM_534 10K	THT	1
Shutdown Pot.	TS53YJ-10K	THT	1
PowerMOS	IRFR220	TO-252	1
Bipolar	BCW66H	SOT23	1
Choke inductor	TL. PISN-101-04	SMD	1
Rectifier diode	BYS10-45	DO2	4
Zener diode	BZT55C5V1	SOD80	1
Bridge diode	1N4148	6030	2
Green LED	LED L-C150GCT	8050	1
Orange LED	LED L-C150ECT	8050	1
100uF Cap	TME CE4700/25A	SMD	1
47uF FB Cap.	TAJD476M016R	D	1
100nF Cap.	C0603C101J5GAC	2070	6
Resistors	According to schematic	6030	
5V stab.	LM7805	TO220	2
12V stab.	LM7812	TO220	1
OPA	LM758	SO8	1

Table 2. Part selection

Four jumpers are also used in design for connection of potentiometer and sensor platform and switch button.

7.3.7. Operating guide

The regulator is built to be easy to operate and prevent operator errors. It can be connected to any 15 to 25V AC or DC power source, preferably 20V DC.

Connection to supply voltage is indicated by an orange LED indicator. Function is started by pressing the start button. Normal function is indicated by green LED. Temperature setting is done by the multiturn potentiometer marked as R_Temp_set. Emergency shutdown temperature is set by SMD potentiometer connected to the comparator.

8. Conclusion

First goal of this work was to determine possibilities of diketopyrrolopyrrole derivates, organic compounds commonly used as red pigments, as sensing layers of hydrogen sensors.

Sensors based on derivates of diketopyrrolopyrrole were evaluated. Derivates marked as U14, U34, U35, U54 and U57 were used as sensing layer. It was determined that all mentioned derivates react to gaseous H_2. U35 derivate displayed most promising results, therefore is considered as a model material in this thesis.

Sensor response to different H_2 concentrations was measured. Also, It was determined that temperature has significant effect on the sensor response. Sensor responses were measured for various temperatures ranging from room temperature to above 100°C. Effects of aging and degradation of sensors were observed. Due to the fact, that sensors display also a visible change of characteristics in air and in N_2, differences between air and N_2 as carrier and purge gases was determined. It was stated, that sensors react to presence of O_2.Melamine barrier layer and its effects on the sensor response were investigated, but it failed to function as an O_2 barrier. Volt-Ampere characteristics of U35 sensor were measured and plotted. Based on these plots existence of a contact barrier affecting system resistivity is supposed. This contact barrier existence was not yet sufficiently clarified.

The goal of the thesis was also to design a simple, low cost and easy to use facility for testing of hydrogen sensors. The designed facility is a static system. Sample gases are administered into the chamber, and then the testing of sensors is performed. This facility can be used for testing of static parameters of sensors. Responses to changing levels of hydrogen, pressure, relative humidity, temperature or concentration of contaminant gases cannot be precisely determined. On the other hand, it is very simple, need not utilize gas analysis equipment (composition of gas is calculated from known volumes of chamber and syringe) and is easy to operate.

In comparison, the dynamic facility enables dynamic analyzes of the sensor. Response testing can be performed. The chamber is flow-through with continuous gas flow. Parameters such as temperature, relative humidity, pressure, and gas concentration can be measured continuously. The facility utilizes a number of complex elements such as the gas chromatography unit. These make the facility a costly piece of laboratory equipment not only concerning the purchase price, but also maintenance costs.

After practical testing of both concepts it is clear that both have their pros and cons. Advantages of the dynamic system are obvious. Repetitive testing, degradation testing, many variables, all done in one test. Due to limitations of the MFCs however, it is hard to achieve very low concentrations of gasses. This can be on the other hand easily done in static mode. The chamber is currently not equipped with a fan, which makes it hard to determine whether the gasses inside are mixed properly. The fan is already on site and can be installed.

Another problem has arisen during the testing, and that is the difficulty of maintaining stable temperature inside the chamber. Regulator circuit was designed to maintain stable temperature for sensor measurement. Temperature was changed during testing by two mechanisms. One of these was that the batteries discharged and were unable to supply sufficient power for heater operation causing a drop of temperature; the other one was slow drift of temperature while power was supplied from laboratory voltage source due to inaccurate setting of temperature and long stabilization time. Also, connection of Ohm-meter during the test caused interference and made constant temperature indication impossible. A study of temperature effects was therefore elaborated to determine effects of temperature fluctuation on sensor output and test results. Also, the sensor platform itself was tested to determine voltage-temperature characteristics of platform. These findings were used to design a regulator circuit for upcoming experiments.

The regulator circuit is based on the idea of balanced bridges where voltage differences are processed by operational amplifiers that determine further operation mode. Both sensor temperature and emergency shutdown temperature can be set by potentiometers. LED indicators indicate power supply connection and circuit operation. Emergency shutdown in case of overheating is implemented to the design. Circuit initialization as well as return to normal function after shutdown is done by a Start button.

Verification of function of the regulator under laboratory conditions and graduation of potentiometers is yet to be done.

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[12] Courtesy of doc. Ota Salyk, Faculty of Chemistry, Brno University of Technology

[13] *O. Salyk*[1]*, J. Vyňuchal*[2]: 3,6-BIS-(4´-PYRIDYL)-2,5-DIHYDRO-PYRROLO[3,4-C]PYRROLE-1,4-DIONE AS HYDROGEN SENSING MATERIAL,

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